Isotopic Exchange of Beryllium Hydride
with Deuterium

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Abstract

Beryllium hydride was isotopically exchanged with deuterium gas to produce beryllium deuteride. Optimum conditions were 1.034 kbar, 240°C, and 16 h hold time. Higher pressures are advantageous since the hydrides decompose into the elements beginning at 250°C with complete decomposition at 300°C. Amorphous beryllium hydride as synthesized by the pyrolysis of di-t-butyl beryllium does not exchange as prepared, but an activation process by milling is required to release organics and create new surfaces. Experiments were done in a static system and in a dynamic scale-up system. D/H ratios were 12:1 with at least three cycles required for >90% conversions.

Introduction

Beryllium hydride (BeH_2) has been synthesized by Ethyl Corporation workers based upon a modification of the Coates[1] and Holley[2] method which gives product purities of 90-98 wt%.[3] The direct synthesis using beryllium powder and hydrogen has been unsuccessful. Beryllium deuteride (BeD_2) can also be prepared by Ethyl Corporation's process using all deuterated organic reactants. However, it is difficult to replace all deuterium atoms in hydrogenated alkyls, and the procedures are slow and costly.

We report a process of producing BeD_2 by activating pyrolysis-process BeH_2 and exchanging the hydride with deuterium gas under pressure and temperature.

Experimental Section

All work was conducted under a moisture-free argon atmosphere. Because of the toxicity of beryllium compounds, a glove box was employed in transferring beryllium hydride and deuteride to and from pressure vessel reactors.[4]

Equipment. The BeH_2-D_2 exchange experiments were carried out using two types of apparatus: (1) an apparatus for parameter studies, and (2) a dynamic scale-up apparatus. The pressure vessel for parameter studies is shown in Fig. 1. A 38-ml capacity pressure vessel was fabricated of Udimet 500 alloy and was fitted with 0.15 cm i.d. 304L-type stainless steel tubing, Autoclave Engineering Co. 2 kbar valves, and a porous 5-μm stainless steel filter. A Marshall Products Co. furnace, 208 V, 15 A capacity, and vertically supported on a drill-press column was used to heat the bottom section of the pressure vessel. The pressure-vessel seal (59° angle male - 60° angle female) was unheated. A Leeds and Northrup Co. Speedomax H Recorder, a series 60 control unit, and a Fincor saturable core reactor maintained temperatures automatically. The temperature of samples was measured with stainless-steel sheath thermocouples inserted into the sample. Pressures were measured with a Baldwin-Lima-Hamilton SR-4 2 kbar pressure cell on the reactor and a 3.3 kbar Heise gauge on the deuterium gas storage supply. A Cenco vacuum pump together with a liquid-nitrogen trap served to evacuate the system prior to admitting D_2 gas. Containers for BeH_2 were made of Pyrex with an orifice to admit gas provided in the ground-glass stopper. Beryllium hydride samples for the static system were 40 mg.

The scale-up experiments were done in a rotating reactor shown in Fig. 2. Figure 3 shows the
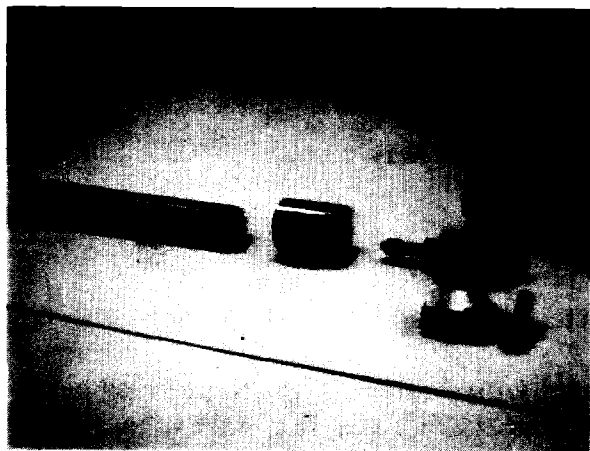
Figure 1. Cold-seal pressure vessel fabricated of Udimet 500 alloy, 0.95 cm i.d. The seal section is unheated, hence the cold-seal designation.
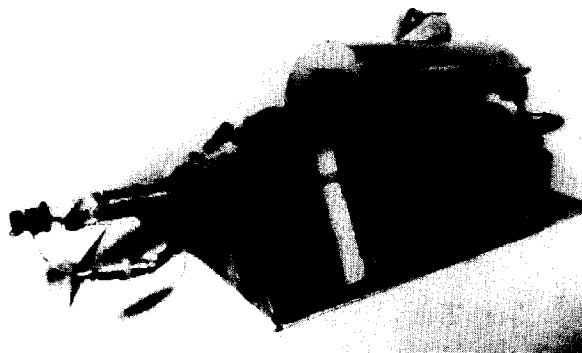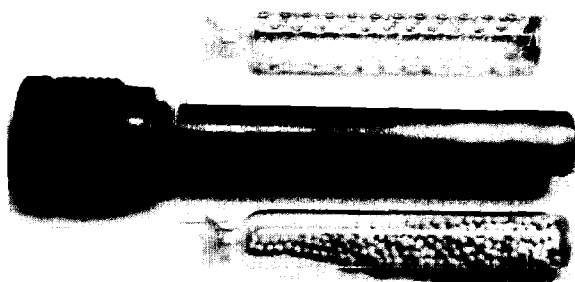

Figure 2. Rotating reactor and heating system.

Figure 3. Canisters for hydride containment.

Figure 4. Amorphous beryllium hydride as produced by the solvent pyrolysis process Mag. 1000X. The small particles range from 5-20 μm; ρ = 0.62 - 0.65 g/cc.

dimpled Pyrex canister for BeH_2 and the stainless-steel housing used to hold the Pyrex canister on the pressure-vessel closure. The canister housings contained porous stainless-steel disks on the ends to allow D_2 gas to enter. The Pyrex tube was also fitted with a porous glass frit. D_2 gas was fed to the reactor through a valve, and the gas-feed line was disconnected prior to start of rotation. Pressure Products, Inc. fabricated the reactor from AISI 4340 steel and lined it with type 316 stainless steel. This reactor has a gross volume of 650 ml and a free-gas void volume of 345 ml after the container is installed. The closure seals consist of a wedge-ring made of Berylco 25, a Viton O-ring, and a Spirolox retainer ring. The reactor is turned at 4 rpm by a sprocket-chain driven by a Vickers, Inc. hydraulic drive motor, No. MRT 3, and a Vickers pump, No. PTR-3. The vessel was externally heated by 10 Chromalox strip heaters made

by E. L. Wiegand Co., No. SE 1405 (R69 HKL) each rated at 500 W at 208 V. The housing was 0.635 cm aluminum plate. Temperatures in the reactor were measured by a Chromel-Alumel sheath thermocouple which rotated with the reactor, and the signals were taken off the thermocouple housing by means of gold brushes made by Airflyte Electronics Co., No. 110-2 CAY. Pressure in the reactor was monitored with pressure transducers with signals taken off of Airflyte Electronics Co. No. 110-6 gold brushes in the same manner as for the thermocouples. Beryllium hydride samples for the dynamic system were 8 g.

Preparation of BeH_2. Amorphous beryllium hydride as prepared by the pyrolysis of di-t-butylberyllium etherate[3] does not isotopically exchange unless it is further activated by milling. Figure 4 shows 95 wt% amorphous BeH_2. The milling is done in a 1.1-liter Abbe ball mill lined

with tungsten carbide using 1.27-cm diameter tungsten carbide balls to avoid contaminating the hydride, although Burundum cylinders, 1.27 cm × 1.27 cm, were also used successfully. The grinding media occupied 30% of the total volume of the mill. About 10 gm of BeH_2 were ground at one time to < 22 μm. Grinding time was 3 h at 125 rpm. A pressure gauge was attached to the ball mill to measure any pressure changes during milling. By knowing the pressure, volume, and gas analysis, we determined the number of moles of each constituent released upon milling.

An alternate activation procedure is to densify the amorphorus BeH_2 at 8 kbar, 180 - 200°C for 1 h in a piston-mold unit and then pulverize the compact to approximately 3.5 μm.

Analytical Measurements. Methods for determination of hydride hydrogen, beryllium alkyls, alkoxides, and chlorides are described in preceeding papers.[3,5] Gas atmosphere compositions were done by mass spectrometry analysis.

Deuterium-Hydrogen Ratio. The yield of BeD_2 is partially dependent upon the D/H ratio used per exchange cycle. In experiments with 40 mg samples, a 1000:1 ratio was used at the highest pressure. In scale-up experiments, the proportion of deuterium to hydrogen was substantially reduced to 12:1.

Deuterium gas was pumped into 1.72 kbar storage cylinders using a Pressure Products diaphragm compressor. The reactors were charged from the storage cylinders.

Isotopic Exchange. Both types of reactors were loaded with BeH_2 in an argon-filled glove box and transferred to a gas manifold for evacuation of the argon with a vacuum pump and subsequent charging with deuterium. The charging pressure was selected so that, after heating we would reach the pressures utilized in isotopic exchange study. Sampling of the pressure-vessel atmosphere and aliquots of samples were taken for analysis. Analysis was made for BeD_2, BeH_2, Be metal, H_2, HD, and D_2 from which the percent exchange could be calculated.

RESULTS

Maximum Yield of BeD_2. The conditions for the maximum conversion of BeH_2 to BeD_2 are summarized in Figs. 5, 6, 7, and 8. Figure 5 was plotted using the peak values in Figs. 6, 7, and 8. Since yield experiments were performed with a restricted number of points, sections of some curves were estimated by drawing the curve parallel to one which contained sufficient data. Operating at 1.034 kbar and 240°C for ~16 h produced opti-
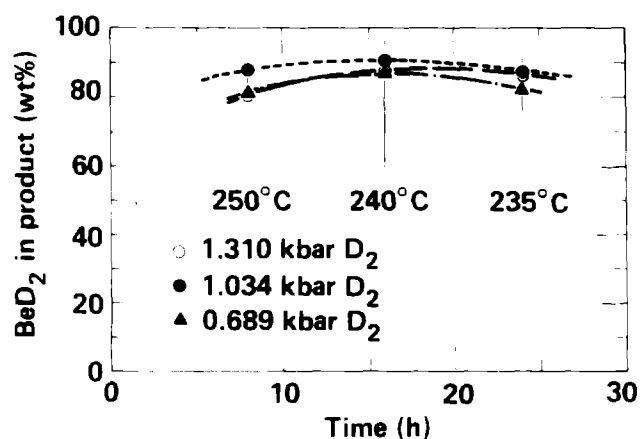
Figure 5. Optimum BeD_2 yield is obtained by operating at 1.034 kbar deuterium pressure, 240°C, 16 h.
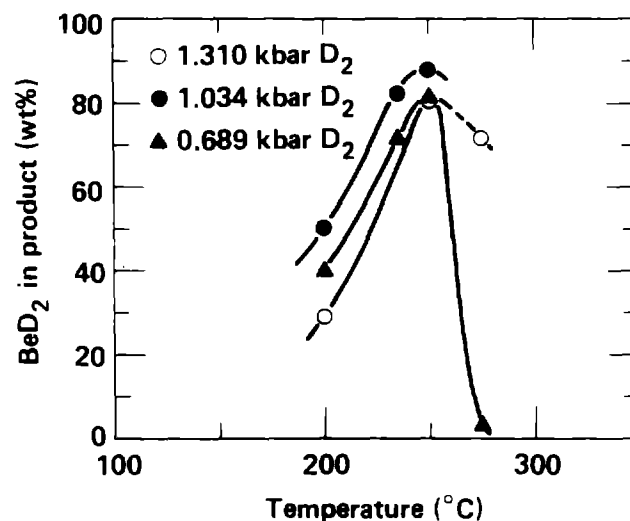
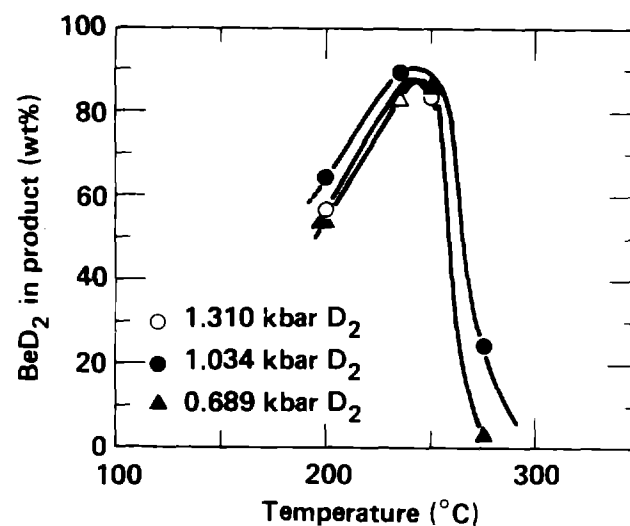Figure 6. Weight percent BeD_2 in product as a function of temperature for 8-h contact time.

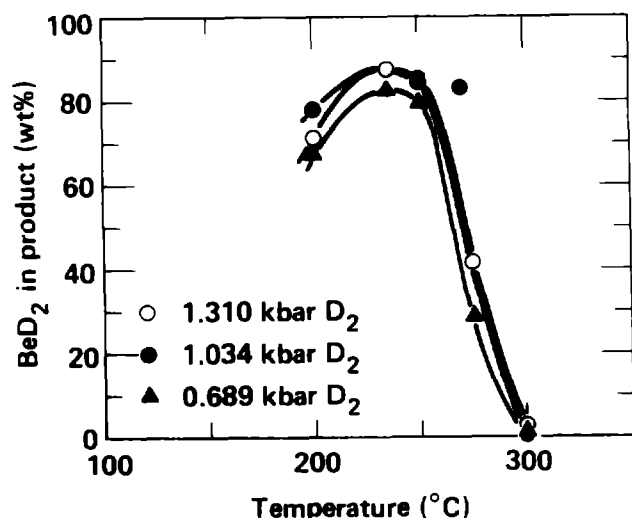Figure 7. Weight percent BeD_2 in product as a function of temperature for 16-h contact time.

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Figure 8. Weight percent BeD_2 in product as a function of temperature for 24-h contact time.
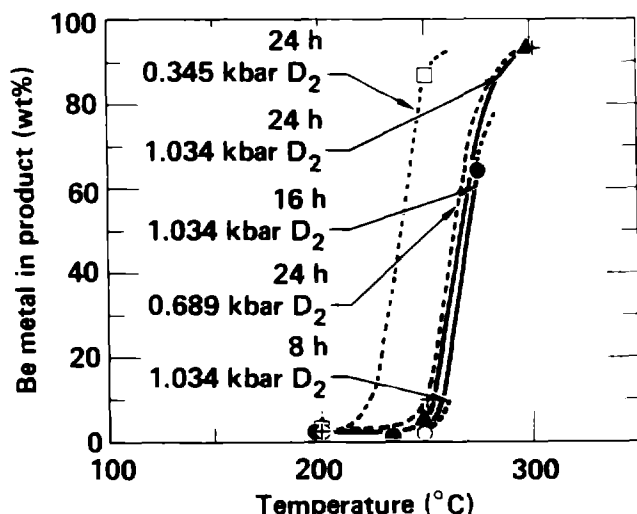

Figure 9. Free beryllium metal in product as a function of temperature at various times and pressures.
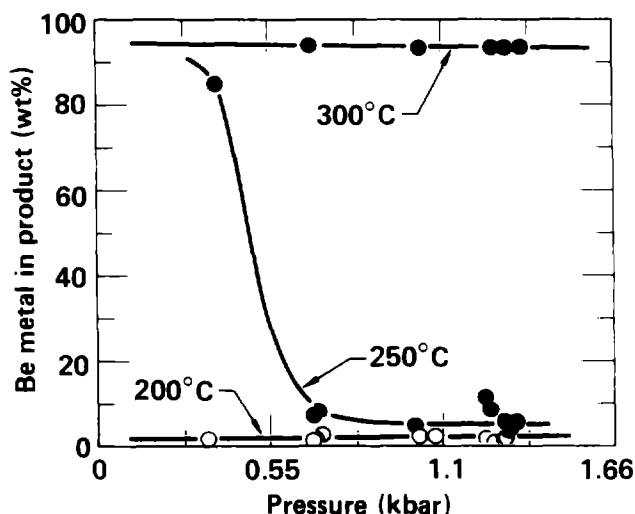

Figure 10. Free beryllium in product as a function of pressure for three temperatures and a 24-h contact time.

mum conversion of 91 wt% BeD_2 from 95 wt% BeH_2 in one cycle. This represents a conversion of 94% to the deuteride. During exchange, the free Be metal content increased from ~2 to ~3 wt%. Since the 1.034 kbar curve is practically flat, slight deviation in time is not critical. Decreasing the time to 8 h at 1.034 kbar while maintaining a temperature of 250°C would decrease the BeD_2 content by 3 wt%. Any decomposition of the hydride to Be decreases the amount of hydride available for conversion to deuteride. The decomposition reaction is not reversible.

Figure 6 shows plots of wt% BeD_2 in the product as a function of temperature for an 8 h contact time, and Figs. 7 and 8 show the results of 16 h and 24 h contact times respectively. We believe that greater pressures, e.g. 1.31 kbar, would provide a larger driving force for exchange but there maybe a barrier to exchange if the released H_2 remains stagnant in the static system.

Figure 9 shows the increase in free Be metal during 8, 16, and 24 h runs for 0.345, 0.689, and 1.034 kbar in a static system. For the 1.034 kbar pressure, decomposition of BeH_2 starts at ~250°C and is completed at 300°C for all times. Figure 10 shows a plot of free Be in the product as a function of pressure for temperatures of 200°C, 250°C, and 300°C and 24 h contact time. At 200°C the BeH_2 is fairly stable.

Scale-up. Limited studies conducted in static apparatus allowed scale-up of the exchange process. Conditions in scale-up approximated the optimum operating values determined in the parameter study, namely, 1.378 kbar, 234°C and 16 h hold time. The higher pressure and lower temperature were chosen to lessen hydride decomposition. The results of a typical experiment are shown in Table 1.

Effluent Gas From Milling. Milling of BeH_2 releases organic gases. A typical sampling of the ball mill atmosphere produced the analysis shown in Table 2. Several reasons for the creation of the active hydride are surmised, which may include (a) distortion of the lattice by grinding, (b) breaking of bonds, (c) creation of fresh surfaces, and (d) removal of screening effect of organics.

Acknowledgments

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Table 1. Experimental Results from 8g Scale-up Experiment of 95 wt% BeH$_2$ with Deuterium Gas.

	Cycle 1	Cycle 2	Cycle 3	Cycle 4[a]
Temperature start °C	RT	RT	RT	RT
Temperature max °C	234	233	234	234
Pressure, charge, kbar	0.993	0.965	0.889	0.883
Pressure at max T, kbar	1.424	1.413	1.434	1.413[b]
Time, RT to shut down, h (hold time, 16 h)	32.2	33.1	25	28
D/H ratio	12/1	12/1	12/1	12/1
Solid Analysis				
BeD$_2$ wt%	88.3	90.5	89.3	93.9
BeH$_2$ wt%	8.7	7.6	7.0	3.2
Be,free wt%	−0.38	1.83	−1.89	−1.34[c]

[a]Sample from the 3rd cycle was reground and returned to the reactor.

[b]There were pressure drops due to gas sampling.

[c]Often the hydrolysis-deuterolysis method for free Be analysis produces negative values. The inconsistency was found to be due to excess H$_2$ or D$_2$ gas either trapped within or adsorbed onto the particles of BeD$_2$.

Table 2. Typical analysis of gas atm. from a ball mill after grinding BeH$_2$ for 3 h at RT. The analysis is on an argon-free basis. BeH$_2$ is 95 wt% pure.

Constituted gas	Volume %
N$_2$[a]	1.86
H$_2$	94.
CH$_4$	0.33
C$_2$H$_6$	3.21

[a]N$_2$ is used in the synthesis of BeH$_2$ as a gas blanket. C$_3$H$_8$, C$_4$H$_{10}$, and C$_5$H$_{12}$ are also often found in small amounts. Degradation of the hydride amounts to about 1 - 2 wt% during a 3 h period. It has been suggested that BeH$_2$ is a polymer, (DTB) · (BeH$_2$)$_x$ · (DTB), $\overline{x}$ = 69.29, with the term DTB at the end of the chain.[6] The grinding process is thought to break this chain, release organic components, and create fresh, active surfaces. The surface area for a 3 h grind is 3.1 m^2/g as determined by B.E.T. using krypton gas.

References

1. Coates, G. E.; Glockling, F. J. Chem. Soc., **1954**, Part 2, 2526; Banford, L.; Coates, G. E. Ibid., **1964**, 5591.

2. Head, E. L.; Holley, C. E., Jr.; Rabideau, S. W. J. Amer. Chem. Soc., **1957**, 79, 3687.

3. Baker, R. W.; Brendel, G. J.; Lowrance, B. R.; Mangham, J. R.; Marlett, E. M.; Shepherd, L. H., Jr. J. of Organometallic Chemistry, **1978**, 159, 123 - 130.

4. Shriver, D. F. The Manipulation of Air-Sensitive Compounds; McGraw-Hill: New York, 1969.

5. Buchholz, J.; Frazer, J. "The Determination of Be Metal and Active Hydrogen in Beryllium Hydride", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-12354, 1964.

6. Mounier, J. "Sur les schemas reactionnels d'une preparation de l'hydure de beryllium", C. R. Acad. Sc., Paris, Serie C, **1967**, 265, 1261 - 1263.